

Crystal structure of ethyl 2-(5-amino-1-benzene-sulfonyl-3-oxo-2,3-dihydro-1*H*-pyrazol-2-yl)acetate

Nadia H. Metwally,^a Galal H. Elgemeie^b and Peter G. Jones^{c*}

^aChemistry Department, Faculty of Science, Cairo University, Giza, Egypt, ^bChemistry Department, Faculty of Science, Helwan University, Cairo, Egypt, and ^cInstitut für Anorganische und Analytische Chemie, Technische Universität Braunschweig, Hagenring 30, D-38106 Braunschweig, Germany. *Correspondence e-mail: p.jones@tu-bs.de

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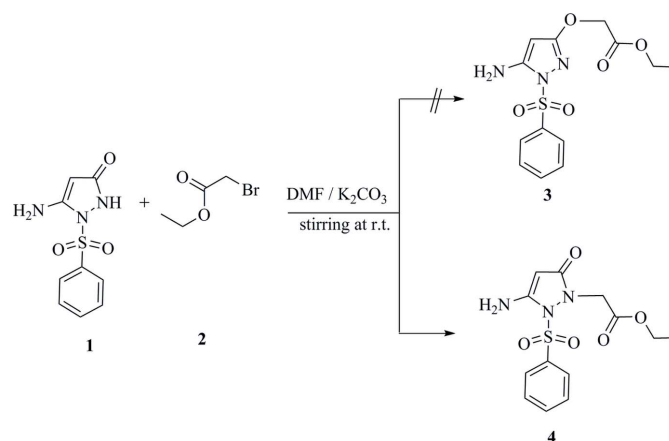
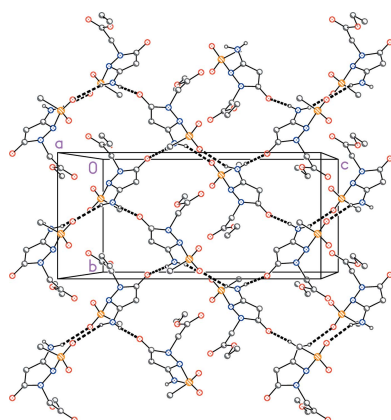
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In the title compound, C₁₃H₁₅N₃O₅S, the two rings face each other in a 'V' form at the S atom, with one N—H...O=S and one C—H...O=S contact from the pyrazolyl substituents to the sulfonyl group. Two classical hydrogen bonds from the amine group, one of the form N—H...O=S and one N—H...O=C_{oxo}, link the molecules to form layers parallel to the *bc* plane.

1. Chemical context

We are interested in the development of innovative synthetic strategies for *N*-sulfonyl- and *N*-sulfonylamino-based heterocyclic ring systems that have found application as new anti-microbial and anti-viral agents (Azzam *et al.*, 2017, 2019*ab*; Elgemeie *et al.*, 2017, 2019; Zhu *et al.*, 2013). Michael *et al.* (2007) investigated the inhibition capabilities of a novel series of our reported *N*-sulfonylpyrazoles (Elgemeie *et al.*, 1998, 1999, 2013) towards the enzyme cathepsin B16. Shyama *et al.* (2009) also identified some of our reported *N*-arylsulfonylpyrazole series to be active inhibitors of the NS2B-NS3 virus. These promising results led our research group to investigate new approaches to other derivatives of *N*-sulfonylpyrazoles, thereby seeking alternative scaffolds for use as promising chemotherapeutics (Azzam & Elgemeie, 2019; Elgemeie & Jones, 2002; Zhang *et al.*, 2020). Accordingly, we synthesized the *N*-1-substituted derivative of *N*-sulfonylpyrazole **1**.



The reaction **1** with ethyl bromoacetate **2** in the presence of anhydrous potassium carbonate in dry *N,N*-dimethylformamide at room temperature produced an adduct for which two possible isomers, the *O*-alkylated or *N*-alkylated *N*-sulfonylpyrazole structures **3** or **4**, were considered. The ¹H NMR spectra of the product revealed the presence of an

Table 1
Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$N3-HO1\cdots O1$	0.866 (19)	2.355 (19)	2.8296 (15)	114.8 (15)
$N3-HO1\cdots O1^i$	0.866 (19)	2.593 (19)	3.3644 (15)	148.8 (16)
$N3-HO2\cdots O3^{ii}$	0.871 (19)	1.961 (19)	2.8257 (15)	171.5 (17)
$C12-H12A\cdots O2$	0.99	2.38	3.0214 (16)	122

Symmetry codes: (i) $-x+1, -y+1, -z$; (ii) $-x+1, y+\frac{1}{2}, -z+\frac{1}{2}$.

amino group at 7.34 ppm and a pyrazole CH at 4.34 ppm, but spectroscopic data cannot differentiate between structures **3** and **4**. The crystal structure determination indicated unambiguously the formation of the *N*-alkylated *N*-sulfonylpyrazole **4** as the only product in the solid state.

2. Structural commentary

The structure analysis confirms the formation of compound **4** (Fig. 1). The molecule displays an intramolecular hydrogen bond of the form $N-H\cdots O=S$, and the intramolecular contact $H12A\cdots O2$ is also quite short at 2.38 Å (Table 1). Accordingly, the two rings face each other in a roughly 'V-shaped' form around the central SO_2 unit, with an interplanar angle of $53.45(5)^\circ$ and torsion angles $C7-C6\cdots N1-N2 = -13.10(10)$ and $C11-C6\cdots N1-C5 = 21.26(11)^\circ$. The corresponding angle $N1-S1-C6$ is the narrowest at S1 (the largest is, as expected, $O1=S=O2$). In the pyrazole ring, the bond $C4-C5$ is the shortest, consistent with a major contribution from the resonance form shown in the Scheme. The exocyclic $C5-N3$ bond is appreciably shorter than the two C–N bonds in the ring. The side-chain atom sequence $C12-C13-O5-C14-C15$ displays an extended conformation. See Table 2 for selected molecular dimensions.

3. Supramolecular features

Two classical hydrogen bonds (Table 1) are observed, one from each hydrogen atom of the amino group; the contact

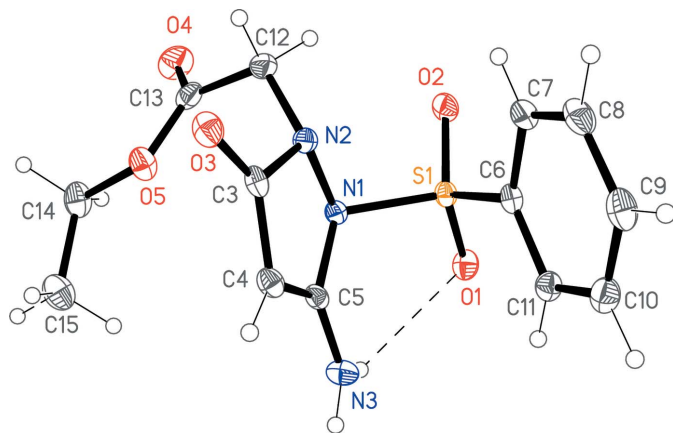


Figure 1
Structure of the title compound **4** in the crystal. Ellipsoids represent 50% probability levels. The dashed line indicates the intramolecular hydrogen bond.

Table 2
Selected geometric parameters (Å, °).

$N1-C5$	1.4305 (15)	$N3-C5$	1.3306 (16)
$N1-N2$	1.4313 (14)	$C3-C4$	1.4184 (18)
$N2-C3$	1.4139 (15)	$C4-C5$	1.3640 (17)
$O2-S1-O1$	120.63 (6)	$N1-S1-C6$	104.30 (5)
$C14-O5-C13-C12$	$-175.81(11)$	$C13-O5-C14-C15$	$158.95(12)$

$HO1\cdots O1^i$, involving the same hydrogen atom that forms the intramolecular hydrogen bond, is however much longer than $HO2\cdots O3^{ii}$. The molecules are thereby connected to form layers parallel to the *bc* plane (Fig. 2).

4. Database survey

A search of the Cambridge Database (Version 5.4; Groom *et al.*, 2016) for the fragment $Ar-SO_2$ bonded to one nitrogen atom of an NNCCC ring (all atoms three-coordinate, any bond orders and any or no other substituents) gave only two hits, our previously reported structures NARCOY ($Ar = Ph$; Elgemeie *et al.*, 1998) and LERBIV ($Ar = p-Tol$; Elgemeie *et al.*, 2013). These are closely related, but the former is pseudosymmetric; for a detailed discussion, see Elgemeie *et al.* (2013). Both bear the same oxo and amino substituents as in the current structure; the latter is, however, substituted at N2,

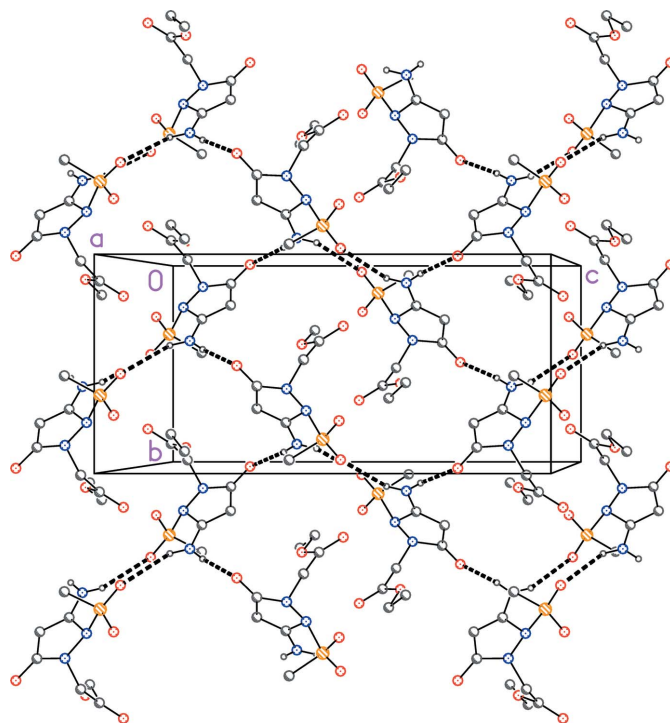


Figure 2
Packing diagram of **4** projected parallel to the *bc* plane. Dashed lines indicate intermolecular hydrogen bonds (intramolecular H bonds are omitted). Hydrogen atoms not involved in this hydrogen bonding system are omitted.

Table 3
Experimental details.

Crystal data	
Chemical formula	C ₁₃ H ₁₅ N ₃ O ₅ S
<i>M_r</i>	325.34
Crystal system, space group	Monoclinic, <i>P</i> 2 ₁ / <i>c</i>
Temperature (K)	100
<i>a</i> , <i>b</i> , <i>c</i> (Å)	9.2139 (4), 8.8122 (4), 18.3486 (7)
β (°)	104.521 (4)
<i>V</i> (Å ³)	1442.22 (11)
<i>Z</i>	4
Radiation type	Mo <i>K</i> α
μ (mm ^{−1})	0.25
Crystal size (mm)	0.35 × 0.30 × 0.15
Data collection	
Diffractometer	Oxford Diffraction Xcalibur Eos
Absorption correction	Multi-scan (<i>CrysAlis PRO</i> ; Rigaku OD, 2015)
<i>T</i> _{min} , <i>T</i> _{max}	0.964, 1.000
No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	74051, 4193, 3708
<i>R</i> _{int}	0.044
(sin θ /λ) _{max} (Å ^{−1})	0.704
Refinement	
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.035, 0.085, 1.11
No. of reflections	4193
No. of parameters	208
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
Δρ _{max} , Δρ _{min} (e Å ^{−3})	0.47, −0.31

Computer programs: *CrysAlis PRO* (Rigaku OD, 2015), *SHELXS97* (Sheldrick, 2008), *SHELXL2017* (Sheldrick, 2015) and *XP* (Siemens, 1994).

so that one fewer hydrogen-bond donor is available and the packing is different from those of the previous structures.

5. Synthesis and crystallization

A mixture of compound **1** (0.01 mol), ethyl bromoacetate **2** (0.01 mol) and anhydrous potassium carbonate (0.01 mol) in *N,N*-dimethylformamide (5 mL) was stirred at room temperature for 2 h. The mixture was poured onto ice–water; the solid thus formed was filtered off and recrystallized from ethanol to give pale yellow crystals in 60% yield, m.p. = 394 K. IR (KBr, cm^{−1}): ν 3330, 3250 (NH₂), 1730 (ester C=O), 1690 (ring C=O); ¹H NMR (DMSO-*d*₆): δ = 1.17 (*t*, 3H, *J* = 7.2 Hz, CH₃), 4.07 (*q*, 2H, *J* = 7.2 Hz, CH₂), 4.34 (*s*, 1H, CH), 4.43 (*s*, 2H, CH₂), 7.34 (*s*, 2H, NH₂), 7.63–7.88 (*m*, 5H, Ar). Analysis

calculated C₁₃H₁₅N₃O₅S (325.34); C, 47.99; H, 4.65; N, 12.92; S, 9.85. Found: C, 48.17; H, 4.84; N, 13.15; S, 9.67%.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. The NH hydrogen atoms were refined freely. The methyl group was refined as an idealized rigid group allowed to rotate but not tip ('AFIX 137'; C–H 0.98 Å, H–C–H 109.5°). Other hydrogen atoms were included using a riding model starting from calculated positions (C–H_{aromatic} = 0.95, C–H_{methylene} = 0.99 Å). The *U*(H) values were fixed at 1.5 (for the methyl H) or 1.2 times the equivalent *U*_{iso} value of the parent carbon atoms.

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Crystal structure of ethyl 2-(5-amino-1-benzenesulfonyl-3-oxo-2,3-dihydro-1H-pyrazol-2-yl)acetate

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Computing details

Data collection: *CrysAlis PRO* (Rigaku OD, 2015); cell refinement: *CrysAlis PRO* (Rigaku OD, 2015); data reduction: *CrysAlis PRO* (Rigaku OD, 2015); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2017* (Sheldrick, 2015); molecular graphics: *XP* (Siemens, 1994); software used to prepare material for publication: *SHELXL2017* (Sheldrick, 2015).

Ethyl 2-(5-amino-1-benzenesulfonyl-3-oxo-2,3-dihydro-1H-pyrazol-2-yl)acetate

Crystal data

$C_{13}H_{15}N_3O_5S$

$M_r = 325.34$

Monoclinic, $P2_1/c$

$a = 9.2139$ (4) Å

$b = 8.8122$ (4) Å

$c = 18.3486$ (7) Å

$\beta = 104.521$ (4)°

$V = 1442.22$ (11) Å³

$Z = 4$

$F(000) = 680$

$D_x = 1.498$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 16307 reflections

$\theta = 2.6$ – 30.3 °

$\mu = 0.25$ mm⁻¹

$T = 100$ K

Tablet, colourless

$0.35 \times 0.30 \times 0.15$ mm

Data collection

Oxford Diffraction Xcalibur Eos
diffractometer

Radiation source: fine-focus sealed X-ray tube

Detector resolution: 16.1419 pixels mm⁻¹

ω -scan

Absorption correction: multi-scan

(*CrysAlis PRO*; Rigaku OD, 2015)

$T_{\min} = 0.964$, $T_{\max} = 1.000$

74051 measured reflections

4193 independent reflections

3708 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.044$

$\theta_{\max} = 30.0$ °, $\theta_{\min} = 2.3$ °

$h = -12 \rightarrow 12$

$k = -12 \rightarrow 12$

$l = -25 \rightarrow 25$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.035$

$wR(F^2) = 0.085$

$S = 1.11$

4193 reflections

208 parameters

0 restraints

Primary atom site location: structure-invariant
direct methods

Secondary atom site location: difference Fourier
map

Hydrogen site location: mixed

H atoms treated by a mixture of independent
and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0304P)^2 + 0.8673P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.47$ e Å⁻³

$\Delta\rho_{\min} = -0.31$ e Å⁻³

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. The NH hydrogens were refined freely. The methyl was refined as an idealized rigid group allowed to rotate but not tip. Other hydrogens were included using a riding model starting from calculated positions.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
S1	0.21827 (3)	0.35269 (3)	0.02872 (2)	0.01371 (8)
N1	0.33782 (11)	0.22191 (12)	0.08270 (6)	0.01304 (19)
N2	0.25215 (11)	0.11750 (12)	0.11476 (6)	0.0142 (2)
N3	0.54212 (13)	0.38935 (14)	0.13239 (7)	0.0187 (2)
H01	0.547 (2)	0.411 (2)	0.0871 (11)	0.029 (5)*
H02	0.602 (2)	0.431 (2)	0.1716 (11)	0.027 (4)*
O1	0.31374 (10)	0.45322 (11)	0.00110 (5)	0.01845 (19)
O2	0.10901 (10)	0.26285 (11)	−0.02197 (5)	0.01864 (19)
O3	0.27967 (10)	0.00832 (11)	0.23139 (5)	0.0201 (2)
O4	0.32627 (13)	−0.17922 (12)	−0.00343 (6)	0.0282 (2)
O5	0.46016 (11)	−0.09414 (11)	0.10922 (5)	0.0206 (2)
C3	0.32177 (13)	0.10511 (15)	0.19250 (7)	0.0151 (2)
C4	0.43781 (13)	0.21500 (15)	0.20999 (7)	0.0159 (2)
H4	0.497420	0.238013	0.258957	0.019*
C5	0.44943 (13)	0.28208 (14)	0.14470 (7)	0.0139 (2)
C6	0.13579 (13)	0.44475 (14)	0.09267 (7)	0.0148 (2)
C7	0.00733 (14)	0.38207 (15)	0.10759 (7)	0.0187 (2)
H7	−0.038852	0.294967	0.081123	0.022*
C8	−0.05126 (15)	0.45024 (17)	0.16212 (8)	0.0219 (3)
H8	−0.137945	0.408731	0.173735	0.026*
C9	0.01580 (15)	0.57863 (17)	0.19982 (8)	0.0223 (3)
H9	−0.025685	0.624603	0.236866	0.027*
C10	0.14298 (15)	0.64049 (16)	0.18388 (7)	0.0206 (3)
H10	0.187588	0.728962	0.209625	0.025*
C11	0.20494 (14)	0.57298 (15)	0.13031 (7)	0.0173 (2)
H11	0.292829	0.613492	0.119539	0.021*
C12	0.20730 (14)	−0.01978 (15)	0.07046 (7)	0.0189 (2)
H12A	0.136124	0.008368	0.022367	0.023*
H12B	0.153689	−0.087254	0.098087	0.023*
C13	0.33651 (15)	−0.10706 (15)	0.05324 (7)	0.0185 (2)
C14	0.59637 (16)	−0.16389 (17)	0.09781 (8)	0.0225 (3)
H14A	0.602432	−0.149340	0.045151	0.027*
H14B	0.596692	−0.274125	0.108255	0.027*
C15	0.72666 (16)	−0.08824 (19)	0.15109 (8)	0.0263 (3)
H15A	0.724485	0.020857	0.140513	0.039*
H15B	0.820526	−0.131624	0.144566	0.039*
H15C	0.720047	−0.104563	0.202995	0.039*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.01461 (14)	0.01428 (15)	0.01147 (13)	0.00241 (10)	0.00185 (10)	0.00165 (10)
N1	0.0123 (4)	0.0133 (5)	0.0126 (4)	0.0006 (4)	0.0014 (3)	0.0012 (4)
N2	0.0141 (5)	0.0141 (5)	0.0136 (4)	−0.0002 (4)	0.0021 (4)	0.0024 (4)
N3	0.0174 (5)	0.0223 (6)	0.0158 (5)	−0.0045 (4)	0.0029 (4)	−0.0011 (4)
O1	0.0216 (4)	0.0181 (5)	0.0170 (4)	0.0021 (4)	0.0074 (3)	0.0038 (3)
O2	0.0191 (4)	0.0197 (5)	0.0137 (4)	0.0022 (4)	−0.0021 (3)	−0.0003 (3)
O3	0.0190 (4)	0.0245 (5)	0.0177 (4)	0.0022 (4)	0.0060 (3)	0.0066 (4)
O4	0.0372 (6)	0.0253 (5)	0.0202 (5)	−0.0032 (4)	0.0037 (4)	−0.0071 (4)
O5	0.0211 (5)	0.0230 (5)	0.0167 (4)	0.0060 (4)	0.0029 (3)	−0.0030 (4)
C3	0.0134 (5)	0.0183 (6)	0.0136 (5)	0.0055 (4)	0.0035 (4)	0.0017 (4)
C4	0.0150 (5)	0.0199 (6)	0.0120 (5)	0.0025 (5)	0.0017 (4)	−0.0010 (4)
C5	0.0112 (5)	0.0154 (6)	0.0144 (5)	0.0025 (4)	0.0019 (4)	−0.0025 (4)
C6	0.0145 (5)	0.0155 (6)	0.0143 (5)	0.0042 (4)	0.0033 (4)	0.0020 (4)
C7	0.0147 (5)	0.0191 (6)	0.0210 (6)	0.0019 (5)	0.0023 (5)	0.0017 (5)
C8	0.0157 (6)	0.0273 (7)	0.0243 (6)	0.0040 (5)	0.0078 (5)	0.0047 (5)
C9	0.0226 (6)	0.0265 (7)	0.0187 (6)	0.0086 (5)	0.0070 (5)	0.0018 (5)
C10	0.0238 (6)	0.0186 (6)	0.0186 (6)	0.0035 (5)	0.0039 (5)	−0.0007 (5)
C11	0.0177 (6)	0.0155 (6)	0.0184 (6)	0.0016 (5)	0.0039 (4)	0.0020 (5)
C12	0.0183 (6)	0.0160 (6)	0.0194 (6)	−0.0026 (5)	−0.0010 (5)	0.0006 (5)
C13	0.0250 (6)	0.0130 (6)	0.0163 (6)	−0.0026 (5)	0.0029 (5)	0.0018 (4)
C14	0.0249 (7)	0.0235 (7)	0.0206 (6)	0.0084 (5)	0.0086 (5)	−0.0015 (5)
C15	0.0221 (6)	0.0333 (8)	0.0242 (7)	0.0047 (6)	0.0074 (5)	0.0012 (6)

Geometric parameters (\AA , $^\circ$)

S1—O2	1.4268 (9)	C6—C7	1.3941 (17)
S1—O1	1.4280 (10)	C7—C8	1.3871 (19)
S1—N1	1.7249 (10)	C7—H7	0.9500
S1—C6	1.7491 (12)	C8—C9	1.388 (2)
N1—C5	1.4305 (15)	C8—H8	0.9500
N1—N2	1.4313 (14)	C9—C10	1.388 (2)
N2—C3	1.4139 (15)	C9—H9	0.9500
N2—C12	1.4583 (16)	C10—C11	1.3883 (18)
N3—C5	1.3306 (16)	C10—H10	0.9500
N3—H01	0.866 (19)	C11—H11	0.9500
N3—H02	0.871 (19)	C12—C13	1.5156 (19)
O3—C3	1.2353 (16)	C12—H12A	0.9900
O4—C13	1.2023 (16)	C12—H12B	0.9900
O5—C13	1.3338 (16)	C14—C15	1.501 (2)
O5—C14	1.4589 (16)	C14—H14A	0.9900
C3—C4	1.4184 (18)	C14—H14B	0.9900
C4—C5	1.3640 (17)	C15—H15A	0.9800
C4—H4	0.9500	C15—H15B	0.9800
C6—C11	1.3926 (18)	C15—H15C	0.9800

O2—S1—O1	120.63 (6)	C7—C8—H8	119.8
O2—S1—N1	104.37 (5)	C9—C8—H8	119.8
O1—S1—N1	104.88 (5)	C8—C9—C10	120.59 (12)
O2—S1—C6	109.90 (6)	C8—C9—H9	119.7
O1—S1—C6	111.12 (6)	C10—C9—H9	119.7
N1—S1—C6	104.30 (5)	C11—C10—C9	119.97 (13)
C5—N1—N2	105.78 (9)	C11—C10—H10	120.0
C5—N1—S1	115.93 (8)	C9—C10—H10	120.0
N2—N1—S1	109.08 (7)	C10—C11—C6	118.73 (12)
C3—N2—N1	107.87 (9)	C10—C11—H11	120.6
C3—N2—C12	119.46 (10)	C6—C11—H11	120.6
N1—N2—C12	114.36 (10)	N2—C12—C13	114.18 (10)
C5—N3—H01	120.9 (12)	N2—C12—H12A	108.7
C5—N3—H02	117.4 (12)	C13—C12—H12A	108.7
H01—N3—H02	121.5 (17)	N2—C12—H12B	108.7
C13—O5—C14	116.94 (10)	C13—C12—H12B	108.7
O3—C3—N2	120.48 (12)	H12A—C12—H12B	107.6
O3—C3—C4	131.97 (12)	O4—C13—O5	125.29 (13)
N2—C3—C4	107.53 (10)	O4—C13—C12	123.59 (12)
C5—C4—C3	108.53 (11)	O5—C13—C12	111.11 (11)
C5—C4—H4	125.7	O5—C14—C15	107.20 (11)
C3—C4—H4	125.7	O5—C14—H14A	110.3
N3—C5—C4	130.69 (12)	C15—C14—H14A	110.3
N3—C5—N1	119.50 (11)	O5—C14—H14B	110.3
C4—C5—N1	109.80 (11)	C15—C14—H14B	110.3
C11—C6—C7	121.97 (12)	H14A—C14—H14B	108.5
C11—C6—S1	119.17 (9)	C14—C15—H15A	109.5
C7—C6—S1	118.76 (10)	C14—C15—H15B	109.5
C8—C7—C6	118.25 (12)	H15A—C15—H15B	109.5
C8—C7—H7	120.9	C14—C15—H15C	109.5
C6—C7—H7	120.9	H15A—C15—H15C	109.5
C7—C8—C9	120.49 (12)	H15B—C15—H15C	109.5
O2—S1—N1—C5	−172.95 (9)	O2—S1—C6—C11	−159.28 (10)
O1—S1—N1—C5	59.29 (9)	O1—S1—C6—C11	−23.16 (12)
C6—S1—N1—C5	−57.61 (10)	N1—S1—C6—C11	89.33 (10)
O2—S1—N1—N2	−53.74 (9)	O2—S1—C6—C7	24.42 (12)
O1—S1—N1—N2	178.50 (8)	O1—S1—C6—C7	160.54 (10)
C6—S1—N1—N2	61.60 (9)	N1—S1—C6—C7	−86.97 (10)
C5—N1—N2—C3	−5.93 (12)	C11—C6—C7—C8	−0.47 (19)
S1—N1—N2—C3	−131.28 (8)	S1—C6—C7—C8	175.72 (10)
C5—N1—N2—C12	−141.43 (10)	C6—C7—C8—C9	0.85 (19)
S1—N1—N2—C12	93.23 (10)	C7—C8—C9—C10	−0.3 (2)
N1—N2—C3—O3	−171.44 (11)	C8—C9—C10—C11	−0.6 (2)
C12—N2—C3—O3	−38.61 (17)	C9—C10—C11—C6	0.97 (19)
N1—N2—C3—C4	7.23 (13)	C7—C6—C11—C10	−0.44 (19)
C12—N2—C3—C4	140.06 (11)	S1—C6—C11—C10	−176.61 (10)
O3—C3—C4—C5	172.70 (13)	C3—N2—C12—C13	−74.54 (14)

N2—C3—C4—C5	−5.75 (14)	N1—N2—C12—C13	55.45 (14)
C3—C4—C5—N3	−179.13 (13)	C14—O5—C13—O4	5.0 (2)
C3—C4—C5—N1	2.02 (14)	C14—O5—C13—C12	−175.81 (11)
N2—N1—C5—N3	−176.57 (11)	N2—C12—C13—O4	−147.96 (13)
S1—N1—C5—N3	−55.56 (13)	N2—C12—C13—O5	32.79 (15)
N2—N1—C5—C4	2.43 (13)	C13—O5—C14—C15	158.95 (12)
S1—N1—C5—C4	123.44 (10)		

Hydrogen-bond geometry (Å, °)

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
N3—H01 \cdots O1	0.866 (19)	2.355 (19)	2.8296 (15)	114.8 (15)
N3—H01 \cdots O1 ⁱ	0.866 (19)	2.593 (19)	3.3644 (15)	148.8 (16)
N3—H02 \cdots O3 ⁱⁱ	0.871 (19)	1.961 (19)	2.8257 (15)	171.5 (17)
C12—H12A \cdots O2	0.99	2.38	3.0214 (16)	122

Symmetry codes: (i) $-x+1, -y+1, -z$; (ii) $-x+1, y+1/2, -z+1/2$.